CALIFORNIA
ENERGY
COMMISSION

ENERGY INNOVATIONS SMALL GRANT PROGRAM
Renewable Energy Technologies

ELECTROSYNTHESIS OF DEVICE QUALITY SEMICONDUCTOR FILMS

FEASIBILITY ANALYSIS

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LEGAL NOTICE

PREFACE

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable and reliable energy services and products to the marketplace.

The PIER Program, managed by the California Energy Commission (Commission), annually awards up to $62 million of which $2 million/year is allocated to the Energy Innovation Small Grant (EISG) Program for grants. The EISG Program is administered by the San Diego State University Foundation under contract to the California State University which is under contract to the Commission.

The EISG Program conducts four solicitations a year and awards grants up to $75,000 for promising proof-of-concept energy research.

PIER funding efforts are focused on the following six RD&D program areas:

- Residential and Commercial Building End-Use Energy Efficiency
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy Technologies
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Strategic Energy Research

The EISG Program Administrator is required by contract to generate and deliver to the Commission a Feasibility Analysis Report (FAR) on all completed grant projects. The purpose of the FAR is to provide a concise summary and independent assessment of the grant project using the Stages and Gates methodology in order to provide the Commission and the general public with information that would assist in making follow-on funding decisions (as presented in the Independent Assessment section).

The FAR is organized into the following sections:

- Executive Summary
- Stages and Gates Methodology
- Independent Assessment
- Appendices
    - Appendix A: Final Report (under separate cover)
    - Appendix B: Awardee Rebuttal to Independent Assessment (Awardee option)

For more information on the EISG Program or to download a copy of the FAR, please visit the EISG program page on the Commission's Web site at:
http://www.energy.ca.gov/research/innovations

or contact the EISG Program Administrator at (619) 594-1049 or email eisgp@energy.state.ca.us.

For more information on the overall PIER Program, please visit the Commission's Web site at http://www.energy.ca.gov/research/index.html.

Executive Summary

Introduction

This project devised a Copper Indium Diselenide (CIS) deposition method that is simpler, less expensive, and more effective than the prevailing methods. The *Electrochemical Molecular Layer Epitaxy* (EMLE) method was developed in order to simplify the synthesis of electronic grade CIS films and reduce fabrication costs for large photovoltaic (PV) modules. The project targeted the energy problem of reducing the capital equipment cost for photovoltaic (PV) modules production in order to make the cost of PV power systems competitive for California ratepayers. It developed this new non-vacuum approach to fabricate high quality thin-film materials for PV modules that could lower the manufacturing costs by over 50% and increase the PV module efficiencies.

The project addressed the PIER subject area of Renewable Energy Technologies. Within that field, this project addresses the cost of manufacturing solar photovoltaic (PV) systems. Worldwide PV markets have been expanding, with sales projected to exceed $12 billion by 2010. PV could provide a large portion of the state's electricity needs without negative impact to the environment, but this potential is limited due to the high initial cost of PV systems. In order to mitigate costs, subsidized buy-down programs have been introduced so that PV power can compete in the current energy market.

This EISG project explored a means to manufacture PV devices at lower cost. It created a non-vacuum fabrication method, specifically targeting the commercially important Copper Indium Diselenide (CIS) PV cell. CIS technology is important because when fabricated with complex, expensive laboratory scale vacuum methods, CIS cells are more reliable and efficient relative to other thin film PV types. Unfortunately, currently existing low-cost non-vacuum methods, suitable for large-area cell manufacturing result in low-grade films, which require further cost-intensive vapor phase treatments. The *Electrochemical Molecular Layer Epitaxy* method integrates the low-cost, large area features of electrodeposition with the atomic level, or nanoscale control of vapor phase epitaxial methods to produce high quality CIS films at ambient conditions from aqueous solutions. The project impacts both the positively doped CIS (*p*-CIS) state of the art solar cell, as well as the new flexible, lower cost negatively doped CIS (*n*-CIS) solar cell being developed.

Objectives

1. Design, assemble and test new apparatus and control software for nanoscale-controlled electrodeposition that eliminates need for vacuum processing.
2. Identify critical deposition parameters.
3. Synthesize binary precursor films.
4. Analyze the thin-films with electrochemical and surface analytical characterization.
5. Extend the investigation to produce ternary CIS absorber layer.
6. Begin a process of commercial readiness

Outcomes

1. A new non-vacuum electrodeposition apparatus, including process control software, was successfully designed, assembled and tested. The introduction of an unconventional thin layer flow cell was the key element that facilitated a precise electrodeposition process.
2. The effects of the standard EMLE deposition parameters of temperature, electrolyte composition, deposition potential, and timing parameters were identified, along with the effect of electrolyte volume.
3. The CuSe superlattice films (binary precursor films) were grown using three different methods, which enabled the identification of the process parameters.
4. A series of samples comprising 500-800 layers deposited on Mo/glass were analyzed and their composition determined. Film composition was tabulated as a function of the process parameter values.
5. This project led to a new method to produce a commercially valuable ternary CIS film, $CuInSe_2$. The results offer valuable insights into the role of process parameters allowing the identification of a new means to incorporate less noble metals in CIS film as required for high efficiency PV cells.
6. A US Patent was granted on May 8, 2001, based on the concepts underlying the new method.

Conclusions

While a fully functioning production line is still five years away, this project advanced the science toward using non-vacuum, electro-deposition for the production of thin film CIS PV cells.

1. The new electrodeposition apparatus and methodology represents an important advancement in electro-deposition process technology. It could allow the substitution of inexpensive electro-deposition hardware for the expensive vacuum deposition processing hardware currently needed to produce CIS thin film PV. Major gains were made in fine control of the electro-deposition process.
2. The new electrodeposition methodology, applied to the task of producing CIS thin film PV, has the potential to eliminate vacuum processing, reduce processing temperature, eliminate the need for multiple electrolytes, and eliminate the need for post annealing step. These potential advantages must be demonstrated in a subsequent development phase.
3. The original objective of this project was to produce a binary precursor film of CuSe using the new EMLE process, however, early success in producing the binary film allowed for the project to be extended to include the successful fabrication of a ternary Cu-In-Se material that constitutes the solar cell absorber layer.
4. Characterization of the fabricated binary and ternary samples confirmed the feasibility of the deposition process to produce high quality layers. This result should support the fabrication of CIS PV films with conversion efficiencies comparable to films produced using the existing expensive process.
5. The results of this research support the conclusion that through the commercialization of the new electrodeposition apparatus and methodology that the fabrication cost of electronic grade CIS films could be reduced by at least 50% for large PV modules.

This EISG project has been timely and instrumental in launching an alternate thin film deposition technology with the potential for lower manufacturing cost. The research team learned how to provide fine control of the electro-deposition process. The EMLE method compares well against other low-cost methods for CIS deposition that are being developed for the current *p*-CIS solar cell, as well as for a new flexible, lower cost *n*-CIS solar-cell. Nearly all other methods need an expensive, hazardous high-temperature selenization second step to produce device quality CIS films. The results are particularly important for the production of low-cost, high-volume flexible solar cells, based on *n*-CIS technology.

Further, the results of this project include a new process representing entry into the field of nanotechnology. This approach of electrodeposition controlled at the atomic level presents a relatively simple, rapid and inexpensive process to create a broad spectrum of complex semiconductor superlattices, heterostructures and quantum well devices. The new findings and their anticipated contribution to photovoltaics and nanotechnology are very important.

Benefits to California

The project performed R&D on technology that holds many potential benefits to California electricity ratepayers and the state economy. The project technology has the potential to:

- Provide California ratepayers with a viable cost-effective PV technology.
- Realize an affordable, reliable, state-of-the-art, clean and safe renewable energy resource for California residents.
- Provide a timely cost-effective renewable energy option for distributed generation to California utilities and ensure energy diversity, quality and reliability in the electricity markets.
- Lead to new in-state jobs and higher tax revenues, thus boosting California's vitality and the overall economy.
- Provide a new developmental entry into the high potential nanotechnology field.

Recommendations

The success of the feasibility study warrants further development of the new deposition method to fabricate a complete solar cell. The next stage will advance the project to:

- Extend the functionality of the design, build and test a prototype deposition apparatus and control system suitable for use in fabrication of a complete *n*-CIS solar cell.
- Advance the EMLE process to optimize the methodology for depositing all components of n-CIS PV cells.
- Automate the equipment and process and produce a quantity of *n*-CIS PV cells for operational evaluation and analysis.
- Because there currently exists a complete infrastructure supporting the manufacture and distribution of the positively doped CIS (*p*-CIS) PV cell, it is also recommended that this project advance the process to synthesize the components of *p*-CIS PV cells.
- Develop a preliminary production readiness plan to produce commercially viable PV module manufacturing equipment.

The EISG project results provide the bases and the directions for future R&D to fabricate a complete PV device. The method will evolve into an inexpensive, integrated system for large-scale manufacturing of efficient PV modules. The scale-up will take advantage of the existing automation and process lines designed for the electroplating industry. The final process will be user-friendly, robust and readily amenable to scale-up for mass production of PV modules.

Stages and Gates Methodology

The California Energy Commission utilizes a stages and gates methodology for assessing a project's level of development and for making project management decisions. For research and development projects to be successful they need to address several key activities in a coordinated fashion as they progress through the various stages of development. The activities of the stages and gates process are typically tailored to fit a specific industry and in the case of PIER the activities were tailored to be appropriate for a publicly funded energy research and development program. In total there are seven types of activities that are tracked across eight stages of development as represented in the matrix below.

Development Stage/Activity Matrix

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Stage 7	Stage 8
Activity 1								
Activity 2								
Activity 3								
Activity 4								
Activity 5								
Activity 6								
Activity 7								

A description the PIER Stages and Gates approach may be found under "Active Award Document Resources" at: http://www.energy.ca.gov/research/innovations and are summarized here.

As the matrix implies, as a project progresses through the stages of development, the work activities associated with each stage needs to be advanced in a coordinated fashion. The EISG program primarily targets projects that seek to complete Stage 3 activities with the highest priority given to establishing technical feasibility. Shaded cells in the matrix above require no activity, assuming prior stage activity has been completed. The development stages and development activities are identified below.

Development Stages:	Development Activities:
Stage 1: Idea Generation & Work Statement Development	Activity 1: Marketing / Connection to Market
Stage 2: Technical and Market Analysis	Activity 2: Engineering / Technical
Stage 3: Research & Bench Scale Testing	Activity 3: Legal / Contractual
Stage 4: Technology Development and Field Experiments	Activity 4: Environmental, Safety, and Other Risk Assessments / Quality Plans
Stage 5: Product Development and Field Testing	Activity 5: Strategic Planning / PIER Fit - Critical Path Analysis
Stage 6: Demonstration and Full-Scale Testing	Activity 6: Production Readiness / Commercialization
Stage 7: Market Transformation	Activity 7: Public Benefits / Cost
Stage 8: Commercialization	

Independent Assessment

For the research under evaluation, the Program Administrator assessed the level of development for each activity tracked by the Stages and Gates methodology. This assessment is summarized in the Development Assessment Matrix below. Shaded bars are used to represent the assessed level of development for each activity as related to the development stages. Our assessment is based entirely on the information provided in the course of this project, and the final report. Hence it is only accurate to the extent that all current and past work related to the development activities are reported.

Development Assessment Matrix

Stages / Activity	1 Idea Generation	2 Technical & Market Analysis	3 Research	4 Technology Develop-ment	5 Product Develop-ment	6 Demon-stration	7 Market Transfor-mation	8 Commer-cialization
Marketing								
Engineering / Technical								
Legal/ Contractual								
Risk Assess/ Quality Plans								
Strategic								
Production. Readiness/								
Public Benefits/ Cost								

The Program Administrator's assessment was based on the following supporting details:

Marketing/Connection to the Market. The reaction of the scientific and PV industry communities to this technology has been enthusiastic. The project has not submitted a preliminary business plan and no commercializer has been chosen. However, business-planning information does exist, projecting market share growth to 2.85% in six years. Further, letters of commitment of funding from commercializers are reportedly in place.

Engineering/Technical. The project met the proposed goals. Following early successes with the deposition apparatus, it was decided that the effort and approach would be extended from a binary compound to a more complex and technologically important ternary material. The ternary material selected for study was $CuInSe_2$ which is used for the solar cell rather than its precursor compound CuSe which was initially studied. The results from this extended effort did affirm the viability and practical utility of the EMLE approach to fabricate tangible PV energy conversion devices.

Legal/Contractual. The Awardee holds patents on the EMLE process as well as on the *n*-CIS technology.

Environmental, Safety, Risk Assessments/ Quality Plans. Although the Final Report addresses the issue of Quality Planning, drafts of various planning documents are evidently not available. Initial drafts of the following Quality Plans are needed prior to initiation of Stage 4 development activity; Reliability Analysis, Failure Mode Analysis, Manufacturability, Cost and

Maintainability Analyses, Hazard Analysis, Coordinated Test Plan, and Product Safety. This information can be prepared as separate documents or as a single document with multiple sections, and it may be a small document at this stage, but it should be created. Significant planning information should be recorded within the Manufacturability, Cost and Maintainability Analyses section, probably multiple pages of information.

Strategic. This product has no known critical dependencies on other projects under development by PIER or elsewhere.

Production Readiness/Commercialization. As previously indicated, a commercializer has not been selected. There are reportedly multiple candidates whose commitment is indicated by letter of intent.

Public Benefits. The PIER program has four public benefit goals. The applicable goal for this research project is:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system.

This project potentially reduces the cost to manufacture PV cells. Lower cost cells could lead to lower cost PV generation systems. Cost effective PV systems can increase the application of this technology and thus reduce the environmental impact of electric generation in California.

This project researched advancements in science meant to reduce the manufacturing costs of CIS PV cells. The National Renewable Energy Laboratory published a paper titled “Issues in Thin Film PV Manufacturing Cost Reduction”, authored by Ken Zweibel. Table 5 - Modified is adapted from Table 5 of this paper, after a private communication with the author. It shows estimated capital costs for various thin film semiconductor deposition processes. The advancements achieved in this project are expected to facilitate semiconductor deposition cost reductions of CIS, column SE, which are presently about $26/m^2. These reductions could result in costs similar to those shown for Electrodeposition CdTe, or about $1.80/m^2 to $4.00/m^2.

Table 5 - Modified			
Process (status)	**SE ($/m^2)**	**Companies**	**Initial Cost ($M) for 100 MW @ 10% Eff.**
Sublimation of CdTe (commercial)	$4.4	First Solar	$31M
Electrodeposition CdTe (pilot line)	$1.8 - $4	BP Solar	$10M - $25M
In-Line a-Si GD (commercial)	$30	Solarex, USSC	$210M
Box Carrier (Batch) a-Si (commercial)	$4	EPV	$28M
High-Rate a-Si (experimental)	$14		$99M
High-Rate CIGS Evaporation (experimental)	$26	Global Solar	$186M
Silicon-FilmTM (experimental)	$2.4	Astro-Power	$16M

Reductions in semiconductor deposition process costs would lead to reduced manufacturing facility costs (shown in the right-hand column of Table 5) and, ultimately, reduced PV module costs.

The estimated module manufacturing cost drop as the production volume and module efficiency increase. As seen from Table A, assuming a low 10% efficiency and low production volume for near term manufacturing, and using the published value of $1.8/m^2 from Table 5, the anticipated manufacturing costs are about $80/m^2. Further development to 15% efficient module and increased production volume, could lower the manufacturing costs to below $30/m^2.

Further costs reductions are anticipated for production of PV modules based on n-CIS since it uses fewer materials and processing steps.

Table A. Manufacturing cost estimate for PV modules based on CIGS films using InterPhases approach

Manufacturing capacity	2MW production	20MW production	Higher Capacity
10% efficiency	$80/m^2	$58/m^2	<<$50/m^2
15% efficiency	$52/m^2	$37/m^2	<<$30/m^2

Note that the above analysis does not place a monetary value on the reduced environmental impact resulting from utilization of this system over alternative manufacturing methods. Neither does it value the improved reliability anticipated from modules produced by this method.

Program Administrator Assessment

After taking into consideration: (a) research findings in the grant project, (b) overall development status as determined by stages and gates and (c) relevance of the technology to California and the PIER program, the Program Administrator has determined that the proposed technology should be considered for follow on funding within the PIER program.

Receiving follow on funding ultimately depends upon: (a) availability of funds, (b) submission of a proposal in response to an invitation or solicitation and (c) successful evaluation of the proposal.

Appendix A: Final Report (under separate cover)

Appendix B: Awardee Rebuttal to Independent Assessment (none submitted)

Appendix A to FAR 99-01

ENERGY INNOVATIONS SMALL GRANT (EISG) PROGRAM

EISG FINAL REPORT

ELECTROSYNTHESIS OF DEVICE QUALITY SEMICONDUCTOR FILMS

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Inquires related to this final report should be directed to the Awardee (see contact information on cover page) or the EISG Program Administrator at (619) 594-1049 or email eisgp@energy.state.ca.us.

Acknowledgement Page

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Table of Contents

Appendices

List of Figures

List of Tables

Abstract

This project developed a new approach to lower manufacturing cost, simplify fabrication and increase photovoltaic efficiencies of thin-film solar cells based on $CuInSe_2$ and its alloys (CIS). Currently, CIS modules fabricated with low-cost, non-vacuum methods exhibit lower efficiency than the vacuum deposited laboratory scale cells. Further, these modules require additional cost-intensive, hazardous, high-temperature selenization. The project developed a revolutionary electrochemical approach for relatively rapid and inexpensive synthesis of electronic grade CIS films, which avoids the high-temperature treatment. The method entailed building a superlattice of semiconductor monolayers by electrodeposition from a single electrolyte. This nanoscale deposition approach extends the utility of epitaxial methods to module fabrication with simpler apparatus and practical deposition rates.

The EISG project designed, constructed, implemented and tested new deposition apparatus. It investigated the reaction mechanisms, identified process parameters and used the data to synthesize CuSe films. The investigation was further extended to synthesize the ternary CIS absorber layer. The layer composition-process parameter correlations revealed crucial information and provided directions to advance the new method for the synthesis of morphologically homogenous, stoichiometric films. The project results can lead to an efficient, reliable and affordable photovoltaic energy conversion device for California ratepayers.

The new approach combines the low-cost, scale-up and environmental advantages of electrodeposition with the atomic level control of epitaxial deposition. The PIER-EISG support provided a timely resource to launch an exciting new enabling technology for thin-film photovoltaics. Its success could propel the CIS photovoltaics into the electric generation market and help alleviate California's electrical power shortage without damaging the environment.

Keywords: photovoltaics, $CuInSe_2$, electrodeposition, low-cost synthesis, thin-film, nanoscale.

Executive Summary

Introduction

The project targeted an important energy problem of facilitating the implementation of low-cost photovoltaic (PV) power for California ratepayers. It developed a revolutionary new approach to fabricate high quality thin-film materials for PV modules that could lower the manufacturing costs by over 50% and increase the PV efficiencies. The project addressed the PIER subject area: Renewable Energy Technologies.

The current energy crises afflicting California has once again focused attention on PV to provide a cheap renewable non-polluting solution to an otherwise intransigent problem. Worldwide PV markets have been expanding, with sales projected to exceed $12 billion by 2010. PV could provide a large portion of the state's electricity needs without causing irreparable damage to the environment. PV is not widely used primarily due to the initial installation costs of PV systems currently at ~$7 per Watt (W), due to the high module manufacturing cost of ~ $4W. Thus the state subsidized buy down programs have been introduced so that PV power can compete in the current energy market.

This EISG studied the feasibility of reducing the high cost of PV systems with an innovative concept to lower the PV manufacturing costs below $1W. It creates a revolutionary fabrication method, specifically targeting the commercially important copper indium diselenide (CIS) PV module. CIS cells are most reliable and efficient relative to other thin film PV cells when fabricated with complex, expensive laboratory scale vacuum methods. Unfortunately, low-cost non-vacuum methods, suitable for large-area module manufacturing, lead to low-grade films, which require further cost-intensive vapor phase treatments.

The project devised a CIS deposition method that is simpler, less expensive, but more effective than the prevailing methods. The method integrates the low-cost, large area features of electrodeposition with the atomic level control of vapor phase epitaxial methods to produce high quality CIS films at ambient temperature and atmosphere from aqueous solutions. The project impacts both the current positively doped CIS (*p*-CIS) solar cell, as well as the new flexible, lower cost negatively doped CIS (*n*-CIS) solar cell being developed by InterPhases.

Objectives

1. Design, assemble and test new apparatus for nanoscale deposition that eliminates the need for vacuum processing.
2. Identify critical deposition parameters.
3. Synthesize binary precursor films.
4. Analyze the thin-films with electrochemical and surface analytical characterization.
5. Produce ternary CIS absorber layer.

Outcomes

1. The project developed a fundamentally new electrochemical process to fabricate semiconductor compounds, engineered on nanoscale.
2. It evolved beyond the initially proposed objective 3 to produce precursor films, to a new objective 5 that produced the commercially valuable CIS films.
3. It decisively established the technical feasibility of the new process from the following developments:
    - A new system was designed and constructed, in conjunction with a new process control system. The configuration, geometry and operation for each of the system components were optimized.
    - The distinguishing features of the new deposition process were identified relative to conventional electrodeposition. The effects of a range of process parameters on the deposit properties were investigated.
    - The special features of the new method were utilized to synthesize CIS thin-films controlled at molecular level, which were then characterized.
4. The results reveal crucial information and provide directions to advance the new method to produce efficient, reliable and affordable solar energy conversion devices.
5. A US Patent was granted on May 8, 2001, based on the concepts underlying the new method.

Conclusions

1. The EISG project advanced the R&D on a radically new concept for thin-film deposition.
2. It developed a practical method to synthesize compound semiconductors; it can potentially simplify the synthesis of electronic grade CIS films and reduce the fabrication costs by at least 50% for large PV modules.
3. We exceeded the proposed project goals, extending the approach to a more complex, technologically relevant CIS ternary material; the results offer valuable insights into the role of process parameters and identify a new parameter for single-step synthesis of multinary compounds.
4. The process is strategically placed against other low-cost methods for CIS deposition that are being developed. Nearly all these methods need an expensive, hazardous high-temperature selenization second step to produce device quality CIS films. Our approach produces high quality films directly in the first step at low temperature, thus avoiding the undesirable second step.
5. The project developed enabling technology to fabricate a critical component for the current *p*-CIS solar cell, as well as for a new flexible, lower cost *n*-CIS solar-cell, being developed by InterPhases.

The PIER-EISG award has been timely and instrumental in launching a revolutionary thin film deposition technology. It led to extremely important and some unexpected results, which we are eager to explore, to create high efficiency PV cells. The results are particularly important for the production of low-cost, high-volume flexible solar cells, based on InterPhases *n*-CIS core technology for building integration and electric vehicles.

Further, this award has enabled our new process to enter the high impact field of 'nanotechnology' at the ground level. This nanoscale electrodeposition approach presents a relatively simple, rapid and inexpensive process to create a broad spectrum of complex semiconductor superlattices, heterostructures and quantum well devices. In view of the importance of the new findings and the anticipated contribution to photovoltaics and nanotechnology, the project definitely warrants further development.

Benefits to California

The project develops public interest R&D that holds many potential benefits to California electricity ratepayers and the state economy. The project technology targets at least three PIER program areas. It has the potential to:

- generate an affordable, reliable, state-of-the-art, clean and safe renewable energy resource for California residents.
- provide California ratepayers with a viable cost-effective PV technology.
- propel the highly promising CIS PV technology into the electricity generation market.
- resolve the current California energy crisis and meet future energy needs without damaging the environment.
- provide a timely cost-effective renewable energy option for distributed generation to California utilities and ensure energy diversity, quality and reliability in the electricity markets.
- forestall the widely unpopular proposal to build new fossil fuel power plants and increase oil drilling in Alaska.
- lead to new in-state jobs and higher tax revenues, thus boosting California's vitality and the overall economy.

Recommendations

The success of the feasibility study warrants further development of the new deposition method to fabricate a complete solar cell. The next stage will advance the project to:

- Design, build and test a prototype deposition apparatus and control system.
- Advance the new process to synthesize the components of *p*-CIS PV cells.
- Develop the method to deposit the components of InterPhases *n*-CIS PV cell.
- Automate the equipment and process for large volume production.
- Develop a preliminary production readiness plan to produce a commercially viable product.

The EISG project results provide the bases and the directions for future R&D to fabricate a complete PV device. The method will evolve into an inexpensive, integrated system for large-scale manufacturing of efficient PV modules. The scale-up will take advantage of the existing automation and process lines in the electroplating industry. The final process will be user-friendly, robust and readily amenable to scale-up for mass production of PV modules.

Introduction

Background and Overview

The Project targets an important energy problem, facilitating the implementation of low-cost photovoltaic (PV) power to California ratepayers. It develops a revolutionary new approach to fabricate high quality thin-film materials for PV modules that will lower the manufacturing costs and increase the PV energy conversion efficiencies.

The project serves at least three of the PIER program areas of interest: (1) Renewable Generation (2) Energy-Related Environmental Research and (3) Strategic Energy Research.

The current energy crises afflicting California has once again focused attention on PV to provide a cheap, renewable, non-polluting solution to an otherwise intransigent problem. PV can provide a large fraction of the state's electricity needs without causing irreparable damage to the environment. PV can cut our utility bills and eliminate insecurities about the current rolling blackouts and electricity price increases. It can conserve our dwindling fossil fuel reserves, reduce toxic emissions and hazardous waste. PV is less widely used primarily due to the initial installation costs of PV systems. The PV module costs remain high particularly for the high efficiency devices.

The EISG project develops innovative concepts to lower the manufacturing costs and increase the efficiencies of thin-film PV modules. It develops a revolutionary electrochemical approach to fabricate high quality absorber films, specifically targeting the commercially important PV modules based on copper indium diselenide and its alloys (CIS). CIS modules exhibit lower efficiency than the laboratory scale CIS cells. The problem is that the complex, expensive laboratory scale methods used to make efficient small cells are not available to module manufacturers.

Lowering CIS PV costs requires a non-vacuum deposition method with low capital investment that is also scaleable, material and energy efficient, high-throughput, amenable to automation and simple to use. Electrodeposition offers these features, but like most low-cost, large-area deposition methods leads to low grade films, requiring further vapor phase treatments. This hybrid approach is neither economical nor suitable for coating large area modules. Nevertheless, a hybrid of electrodeposition/vacuum evaporation led to over 14% efficient cells [1].

Electrodeposition could be a promising approach if the high temperature vapor phase steps were avoided. Chemical and electrochemical atomic layer epitaxy were recently introduced to synthesize binary compounds on single crystals from separate solutions [2-5]. The method is however impractical for manufacturing large photovoltaic modules; such devices need low-cost, large-area, high-throughput deposition. Also, the atomic layer epitaxy is unsuitable for deposition of copper selenide (CuSe) and many other compounds, because it leads to the re-dissolution of one metal (Cu) during deposition of the next (Se).

Project Objectives

The overall project objective was to develop a distinctly different approach: *electrochemical molecular layer epitaxy* (EMLE) to simplify the synthesis of electronic grade CIS films and reduce fabrication costs for large PV modules [6,7].

Specific EISG project objectives:

- Design, assemble and test new apparatus for the EMLE deposition.
- Identify critical deposition parameters.
- Develop the EMLE approach to deposit high quality CuSe film.
- Analyze the thin-films by electrochemical characterization and surface analysis.

The economic objectives:

- Lower capital equipment costs.
- Simplify the deposition process for large area modules.
- Lower fabrication cost for high quality CIS PV modules.

New objectives that emerged during the project:

- Develop the EMLE approach to synthesize the ternary $CuInSe_2$ absorber layer.
- Extend the scope of EISG project objectives 1-4 to investigate the reaction mechanisms, synthesis and characterization of $CuInSe_2$ films.

The Project Approach section discusses the reasons for the new direction.

Report Organization

This report is organized to briefly:

- Outline the concepts underlying the new EMLE approach
- Describe new deposition apparatus
- Investigate the reaction mechanisms
- Report the results of the synthesis and characterization of the first Cu-In-Se films synthesized by the EMLE method and
- Present conclusions and suggestions for future work.

Project Approach

The EMLE approach entails the successive electrodeposition of monolayers of a compound from a single electrolyte to form a superlattice [6,7] as shown in Fig. 1. The approach is designed to produce morphologically homogenous films with self-regulating, computer synchronized sequence of flow, equilibrium and deposition from a thin electrolyte layer in a flow cell.

The approach is based on fundamental concepts regarding the nucleation process during electro-deposition. It integrates fundamental electrochemistry concepts of underpotential and diffusion layer deposition with a new concept of molecular layer formation to create a remarkably simple but powerful technique that could lead to cutting edge thin-film technology.

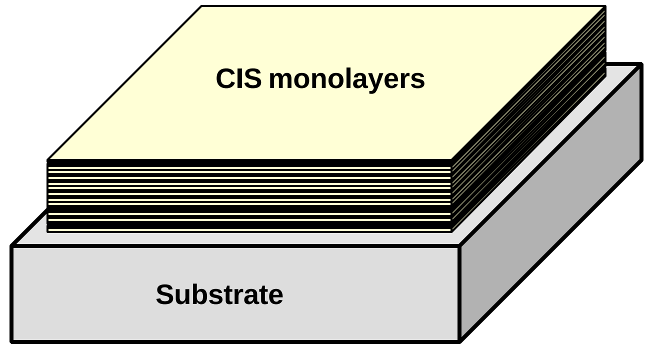

Figure 1. Multiple CIS monolayers formed on a substrate by the EMLE method.

Project Work Plan

The project work plan included design and development of (i) the new deposition apparatus and (ii) the EMLE deposition process. The following tasks (1-4) were performed to determine the feasibility of the EMLE approach:

1) Design and test new apparatus for molecular layer electrodeposition.
The major effort during the project period was devoted to this task to design, construct and assemble the several components of the deposition equipment and develop the control software for its efficient operation.

2) Identify the deposition parameters using electrochemical methods.
Electrochemical techniques, including rotating ring-disk voltammetry, multipulse amperometry, coulometry and potential pulse techniques were used to accomplish this task

3) Design control steps and instrumentation to develop the EMLE approach for CuSe film.
Using the results of task 2, the software was programmed to deliver effective sequences of control steps to generate voltage pulses and delay times as appropriate. An electronic circuit was designed to work in unison with the program.

4) Characterize the films using electrochemical and surface analytical methods.
Rotating ring-disk electrode methods were used to identify the various reactions. Electron microprobe analysis was used to characterize the EMLE synthesized films.

The deposition system development, modifications and improvements and the testing procedures undertaken are summarized in the 'Project Outcomes' section for brevity and clarity.

Project Scope Expansion

Although the long-range project goal was to synthesize the $CuInSe_2$ absorber material for the PV modules, the EISG project planned to demonstrate the EMLE method feasibility with a less complicated binary compound, CuSe. However, in the final quarter two issues, the new federal initiatives and certain project results led to some changes in the project direction and scope.

The EMLE project presented a timely response to new federal initiatives. It addressed National goals as described in *"National Nanotechnology Initiative: Leading to the Next Industrial Revolution".* The last Administration made Nanotechnology a top priority and emphasized its profound impact on our economy and society in the early 21st century. This EISG award has enabled our EMLE concept to enter this high impact field at the ground level. In view of the far-reaching effects of the EMLE approach, the design, compilation and implementation of the new experimental apparatus were prioritized relative to the materials.

Following new developments in the deposition apparatus, we decided to extend the EMLE effort to the synthesis of the ternary material $CuInSe_2$ that is the actual component of the solar cell rather than its precursor CuSe. Even though this effort was not part of the EISG proposal, the results affirm the viability and practical utility of the EMLE approach to fabricate a tangible PV energy conversion device. This final report primarily describes the work done on tasks 1-4 during the 6th quarter, on the ternary Cu-In-Se system.

Project Outcomes

Task 1 - Design and Testing and Optimization of Deposition Apparatus

Task 1 designed, developed and implemented rather complex and elaborate apparatus based on a set of new concepts for the deposition of compound semiconductor films. The final version of the deposition equipment for EMLE is shown in Fig. 2. Its principal components include:

1. A thin layer flow cell, constructed with the assistance of Eltron Research.
2. A three-way solenoid distribution valve and a Masterflex perilstatic pump comprising a variable speed L/S pump drive, an 'Easy-Load' pump head, tubing, connectors and adapters, for delivery and exchange of solutions with the deposition chamber.
3. Electrolyte reservoirs and waste electrolyte container connected to the deposition chamber through feed lines.

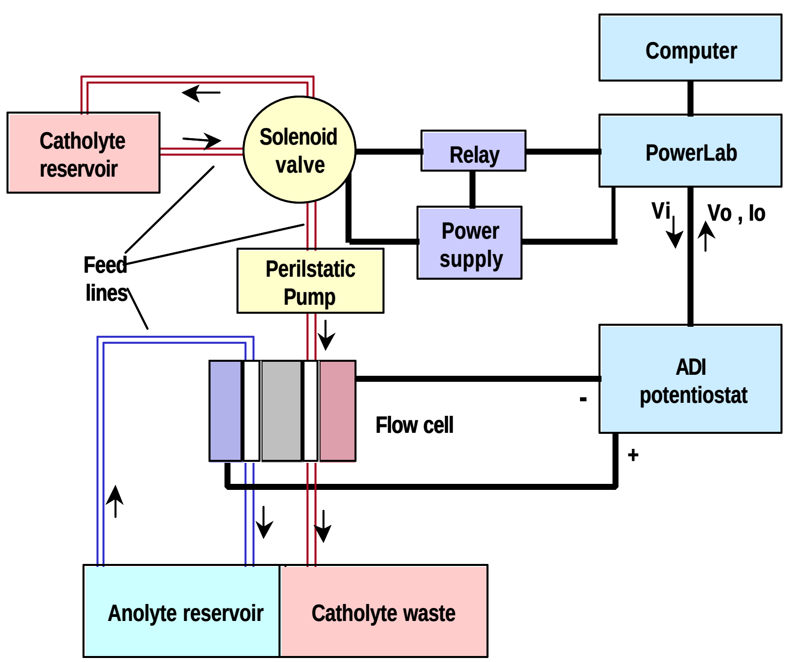

Figure 2. Schematics of experimental set-up developed for EMLE synthesis

4. Powerlab potentiostat recording-control unit and process control software to synchronize the delivery, equilibration, deposition and monitor the deposition parameters.

The flow cell is the central element of the experimental apparatus. It provides a large surface area electrode and a narrow gap for solution flow through the cathode compartment. The narrow gap confines the reactant ions within a thin solution layer, which establishes equilibrium instantly with the electrode surface. It provides each reactant ion immediate access to the electrode surface for uniform nucleation, promoting epitaxy. Quiescent deposition avoids mass transport and flow pattern complications, thus preventing 3-dimensional nucleation and polycrystallinity.

A separator membrane separates the anode compartment. The anolyte is circulated through a separate circuit to prevent interference from anode reaction products. The solenoid valve controls the flow of the catholyte into the cell. The pump speed regulates solution flow rate. A delay time introduced after each filling equilibrates the electrolyte. The catholyte flushes out after the deposition of a molecular layer. The anolyte solution is circulated in a closed circuit to prevent gas accumulation in the anode compartment. The substrates used were Mo/glass, C, Au or Pt coated Cu foils. The counter electrode was Mo/glass, Pt or Ti foil. SCE or a Cu wire measuring the solution redox potential served as reference electrodes.

Task 2 - Deposition Parameters and Reaction Mechanism for Cu-In-Se system

Many alternate reaction paths and products can occur in an electrolyte comprising Cu, In and Se ions. The compounds formed depend primarily on the reaction potential and to a large extent on the relative metal ion concentration ratio in the electrolyte. Controlling the kinetics of competing reactions is essential to obtain a stoichiometric film. The EMLE approach controls kinetics by limiting the solution volume in addition to the standard parameters, e.g., temperature, electrolyte composition and deposition potential [6].

The standard experimental parameters for EMLE deposition: temperature, electrolyte composition, deposition potential, equilibration time and layer deposition time, were investigated by conducting *in-situ* coulometric and voltammetric studies of redox reactions for Se, Cu and In based electrolyte systems using (a) a conventional cell, as well as (b) the thin layer deposition cell [Appendix I]. Distinctly different features between the 2 deposition systems were identified. EMLE for CIS films takes advantage of these unique features, the self-limiting reactions and the low free energy of -254 kJ/mol [13] for CIS formation to control the film stoichiometry

Task 3 - EMLE synthesis of CuSe and $CuInSe_2$ thin-films

The voltammetric data obtained in Task 2 provided the process parameters for CIS deposition. The CIS films were grown with a synchronized solution flow, equilibration and deposition sequence. Molecular layer deposition was monitored by tracking the current transients during deposition. This information derived was used to control the electrolyte flow (or stirring) rate and equilibration time.

The Task 3 results were in agreement with the voltammetric data of Task 2. Distinct differences were observed in the current output generated in bulk solution in a conventional cell and in the thin layer flow cell. The differences were manifested primarily during the anodic segment of the waveform which we attribute to the dissolution of specific binary phases in the two situations.

Task 4 - Characterization of Electrosynthesized Films

This first study of EMLE synthesis explored a variety of experimental parameters for EMLE deposition, including: electrolyte composition, deposition potential waveform, equilibration time, layer deposition time, temperature, stirring or flow rate between layer deposition. The composition of a series of samples comprising 500–800 layers was determined with electron microprobe analysis. The number and types of monolayers deposited during each pulse are deduced from the net charge density/pulse and charge density for monolayer of Se, CuSe, Cu_2Se and $CuInSe_2$ monolayers. The samples had excess of CuSe phase as anticipated for electrodeposition from bulk electrolyte. The CuSe content was related to the deposition potential, the deposition technique and the charge layer.

Task 5 - Final Report

A synopsis of the results of Tasks 1 through 4 are presented in this report. A detailed technical report is included in Appendix I. It contains a description of the deposition mechanism for the various elements and compounds, the deposition process and an analysis of the deposited films.

Conclusions and Recommendations

Conclusions

The EISG project demonstrated the feasibility of a new low temperature deposition approach for compound semiconductor thin-films. The project results have been very promising, substantially advancing the R&D on a very new EMLE concept for thin-film synthesis. The results suggest that the EMLE approach has the potential to simplify the synthesis of electronic grade CIS films and reduce fabrication costs for large PV modules. The key conclusions that support our assessment are drawn from the results presented in the 'Project Outcomes' in section 3 and Appendix I:

1. A practical new deposition system was developed, for the EMLE synthesis of CIS films at room temperature. It included the construction, assembly and implementation of new apparatus, and the optimization of the configuration, geometry and operation for each of the system components.
2. Voltammetric investigations reveal that different reaction mechanisms for CIS formation are prevalent in bulk electrolytes and in a thin solution layer. Elucidation of reaction mechanisms identified the distinctly different process parameters associated with the new system, relative to conventional electrodeposition apparatus. These parameters provide the crucial molecular level control necessary to synthesize homogenous films for CIS PV devices in the next development stage.
3. This first study of applying EMLE concepts to thin-film synthesis provides valuable insights into the role of various deposition conditions that could lead to a practical method for the deposition of a ternary compound.
4. The results of composition and process parameter correlation reveal important information and provide directions for the EMLE synthesis of morphologically homogenous CIS layers.

5. The EMLE method offers many advantages over conventional electrodeposition. It avoids the post-annealing step needed for conventionally electrodeposited films. It also eliminates the use of multiple electrolytes, rinse cycles and elaborate deposition apparatus required for atomic layer epitaxy. Thus, it extends the utility of epitaxial deposition to fabricate devices with simpler apparatus and practical deposition rates.
6. The new research results offer the first indication for the viability of the EMLE technology for commercial fabrication of PV modules.
7. The work performed has exceeded the proposed project goals, extending the approach from a binary compound to a more complex, technologically relevant CIS ternary material. The first feasibility study provides valuable insights into the role of various process parameters.
8. The first demonstration of the EMLE synthesis of CIS films has been a major milestone for thin-film deposition technology. The EMLE project results received enthusiastic reviews from the PV community at the recent national ACS (S. Diego) and MRS (S. Francisco) conference symposia.
9. The EMLE project is strategically placed against the low-cost methods for CIS deposition under development at other companies. Our approach offers several competitive advantages, primarily because it deposits high quality semiconductor films directly in the first step at low temperature. Thus, it avoids the expensive and hazardous second step of high-temperature selenization. Nearly all other low-cost deposition methods need the second undesirable step to convert poor quality precursors into semiconducting films.

The PIER-EISG award has been well-timed and instrumental in launching this revolutionary technology. The project method has evolved successfully beyond the initial proposed approach with the implementation of new experimental set-up, state-of the art electrochemical equipment and software. Extending the project scope from depositing binary CuSe compounds to a ternary CIS compound led to the most important result for this project — a new means to incorporate the less noble metals in CIS film as required, for high efficiency PV cells.

Further, this award has enabled our EMLE concept to enter the high impact field of 'nanotechnology' at the ground level. The EMLE approach could potentially be an enabling technology for nanomaterial synthesis. In view of the importance of the new findings and the anticipated contribution to photovoltaics and nanotechnology, the project definitely merits further development.

Recommendations

The recommendations for the next stage for this project include optimizing the EMLE method to produce high quality thin-films and extend the approach to other materials to produce high efficiency solar cells. Specific objectives have to be accomplished to advance the EMLE technology to the next stage:

1. Design and build a prototype deposition system. The new deposition apparatus design and operation will evolve from the specifications and cost goals stated for the completed project. Further modifications are necessary to the experimental apparatus, the control circuitry and fine-tuning of the deposition cell dimensions.

2. Identify the process parameters to synthesize stoichiometric absorber films for the *p*-CIS cell, e.g., $CuInGaSe_2$, $CuInGa(SSe)_2$.
3. Identify the process parameters to synthesize stoichiometric absorber films for the *n*-CIS cell (e.g., $CuIn_3Se_5$) to produce high efficiency PV cells.
4. Identify process parameters and equipment configurations to construct complete PV devices.
5. Determine composition, microstructure and opto-electronic properties of the electrosynthesized films and their relation to process parameters.
6. Develop the preliminary production readiness plan, including the critical production process, equipment, facilities and person-power needed to produce a commercially viable product.

The EISG project results provide the bases and directions for future R&D for the EMLE synthesis of device-quality absorber layers and other cell components to fabricate the complete PV device.

In addition, the EMLE method will evolve into an integrated system for manufacturing efficient inexpensive PV modules [6]. The method is rapid, user-friendly and amenable to large-scale fabrication of PV modules. Its scale-up takes advantage of the existing automation and process lines in the electroplating industry and commercial modular flow cell units, as shown in Fig. 3. These cells can be stacked to fabricate several PV modules simultaneously. The CIS PV module can thus be batch-processed at a low-cost of < $1/Wp, as envisioned in Stage 1.

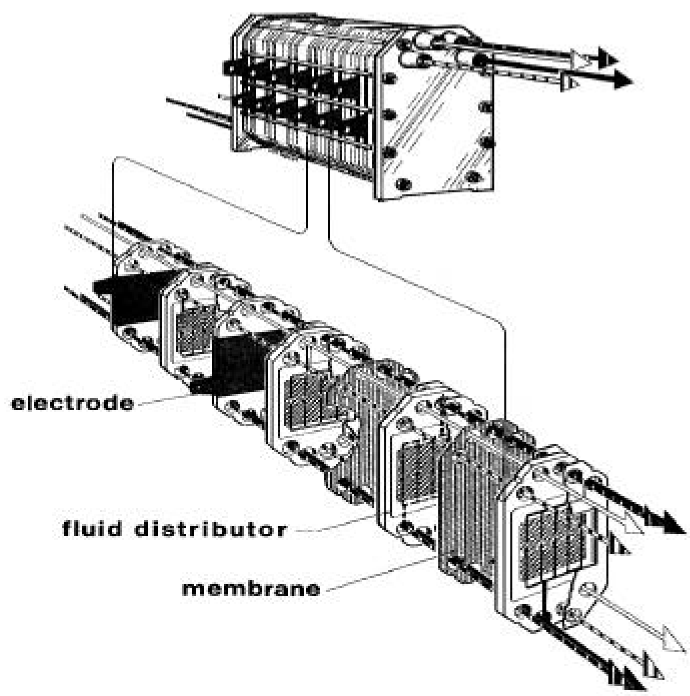

Figure 3. Commercially available equipment for EMLE svnthesis of PV modules.

Benefits to California

The project presents an inexpensive, user-friendly, environmentally benign high throughput process for manufacturing PV modules. It simplifies manufacturing and reduces module fabrication costs to < $1, facilitating the implementation of low-cost PV power to California ratepayers. This project introduces a new fabrication method that can dramatically reduce the initial outlay for PV modules. This method, when combined with InterPhases core technology for *n*-CIS flexible solar cell fabrication further reduces costs. The *n*-CIS cell configuration uses fewer components, fewer processing steps and less packaging than the current *p*-CIS cell. It also uses an unconventional production approach that allows large-scale batch processing with the same equipment used in the laboratory. Its affordability and versatility will allow new applications in building integration and electric vehicles. Current cost projections suggest a module cost of $0.83 for a 2MW and $0.58 for a 20MW production capacity.

At 2200 sun peak hours/year, California offers the best climate for PV. But at present PV needs substantial subsidies and rebates to compete with utility power, Columns 1 and 2 in Table I [18]. InterPhases' low cost technology expects to reduce PV costs to compete with utility electricity prices for existing buildings, without the $3 buy-down subsidy. It would be even more economical for use in new construction where the flexible solar cell would replace conventional building elements (roof tiles, facades, windows, shading devices). In this case our technology can be cost competitive without the 15% tax rebate.

Table I. Economic analysis of grid-connected PV for CA with 2200 sun peak hours/year

Option	Current PV Technology		InterPhases Technology	
	1. No credit	2. CA buy-down + 15% tax rebate + 20-year payback	3. BIPV for old construction + 15% tax rebate + 20-year payback	4. BIPV for new construction + 20-year payback
Module cost ($/W)	$4	$4	$1	$1
Installed cost ($/W)	$7.00	$7.00	$4	$3.55
Capital recovery factor	0.13	0.05	0.05	0.05
Subsidy	0	$3.00 + 15%	15%	0
Electricity price	$0.14/kWh	$0.14/kWh	$0.14/kWh	$0.14/kWh
PV electricity cost	$0.41/kWh	$0.134/kWh	$0.134/kWh	$0.134/kWh

The EISG grant provided a well-timed resource to initiate the EMLE project. It helped launch an exciting new PV technology that could resolve the energy problems facing California without causing irreparable damage to the environment. The project leads to an affordable, non-polluting electricity-generating device for California ratepayers. PV affordability provides a timely cost-effective energy option to the California utilities during the current energy crises. It can eliminate the need to build additional pollution-causing power plants or import natural gas, and reduce hazardous chemical waste disposal in California's landfills.

In addition to the cost benefits, PV electricity provides non-tangible public benefits in terms of clean environment, improved health and safety. The EMLE project technology offers even further environmental benefits, both to the utility worker and to the California ratepayer. The safe, simple, electrochemical manufacturing greatly minimizes hazardous toxic vapor-phase reactants, organic solvents and solid waste. It will impact the local and state economies and expand the RD&D knowledge base.

Since the start of this EISG contract, California has received the following benefits:

The project has created a new scientific information base, which impacts the material science, PV and energy policy-making entities. A new U.S. Patent based on the concepts proposed for the

EMLE project was granted on May 8, 2001. New information about a novel method for producing low-cost solar cells, derived from EISG project results, has been disseminated to the PV industry and scientific community at two California-based technical conferences. The PI presented the following papers:

- "Solution-based Processes for Processing $CuInSe_2$ Thin Films", Symposium on "Thin Film", American Chemical Society Meeting, S. Diego, April 1-4, 2001.
- "Molecular Level Approach for Low Temperature Synthesis of $CuInSe_2$ Films," Symposium H, 'II-VI Chalcogenide Semiconductor Materials', Materials Research Society Conference, S. Francisco, April 14-20, 2001.

The papers generated very enthusiastic response within the scientific community and the PV industry.

The EMLE project has far-reaching effects for the development of the exciting new field of nanotechnology. The EISG project has enabled our nanoscale processing EMLE technology to enter the nationally important area at ground level.

The anticipated savings in the California subsidies alone far outweigh the California Energy Commission cost outlay of $75,000 for this project by several orders of magnitude. The anticipated non-tangible benefits from the project further enhance the public benefit-cost ratio.

Development Stage Assessment

Table II displays the Stage Activity of our EISG project, which has been completed to Stage 3 (Research and Bench Scale Testing).

Table II. Project Development Stage Activity Matrix

Stages / Activity	1 Idea Generation	2 Technical & Market Analysis	3 Research	4 Technology Development	5 Product Development	6 Demon-stration	7 Market Transfor-mation	8 Commer-cialization
Marketing								
Engineering / Technical								
Legal/ Contractual								
Risk Assess/ Quality Plans								
Strategic								
Production Readiness/								
Public Benefits/ Cost								

Marketing Activity

Cost effective CIS PV technology can meet the needs of a rapidly changing energy marketplace. The EISG project impacts the manufacturing cost for the established *p*-CIS PV technology as well as the InterPhases *n*-CIS technology. *p*-CIS technology is in pilot plant stage at several PV companies. The CIS companies are excited at the prospect of expensive vacuum methods with our low-temperature CIS deposition method with its many potential benefits. They encouraged us to speed up its commercial availability

Our *n*-CIS flexible solar cell is even more affordable and versatile. It can penetrate new markets for building integration, electric vehicles, mobile and space systems. Funding commitment letters of intent from our potential commercializers are in place. InterPhases plans joint ventures with the PV industry to manufacture and market the *n*-CIS cell. Its current business plan includes a 2 year development phase leading to a 100kW pilot plant, the construction of a 2MW plant in 2004 and a 20MW plant in 2006 for large scale manufacture of *n*-CIS PV. The plan projects worldwide PV market shares of 0.4% in 3 years and 2.85% in 6 years. In the interim period, the company plans to license spin-off technologies generated from this project.

Engineering/Technical stage

As noted, this effort is a critical component of a larger project that features a new flexible, low-cost *n*-CIS solar cell, which was developed exclusively by InterPhases with private and government funds. Previously completed technical milestones include:

- 12% efficient & stable *n*-CIS solar cell.
- *n*-CIS thin-film cell fabrication method.
- Electrodeposition methods for CIS and $CuISe_3$.
- New $CuIn_3Se_5$ absorber with solar-matched bandgap for *n*-CIS cell.

The EISG project established an important technological milestone in the progression of the *n*-CIS project to the energy market. It demonstrated the technical feasibility of a new simpler and cost effective deposition method and system. The special attributes of the new method were exploited to synthesize CIS films. The next development stage 4 will exploit the EISG project results in the fabrication of *n*-CIS PV cell. In contrast to the current *p*-CIS PV technology, InterPhases' *n*-CIS flexible cell reduces the number of components and processing steps. This reduces its development period and simplifies large scale manufacturing. Three key patents, 30+ technical publications and successful demonstration of six SBIR grants from NSF, DOE and BMDO validate the *n*-CIS technology. It justifies advancing to Stage 4.

Legal / Contractual

A U.S. Patent application based on the concepts underlying the EMLE project was filed on Feb. 8, 1999. The patent, No. 6228243, entitled, "Electrochemical synthesis of crystalline compounds or alloys", was granted on May 8, 2001. Two previous patents, US Patent 4,601,960 (1986) and US Patent 5,286,306 (1994) cover certain portions of the total *n*-CIS project.

Risk Assessment / Quality Plans

The EISG project is specifically designed to simplify PV module manufacturing and lower costs for the established p-CIS cell and our n-CIS cell. Most importantly, the method eliminates the hazardous cyanide etching and selenization steps required with all other CIS deposition methods.

The project offers safe and simple electrochemical manufacturing, which greatly minimizes hazardous toxic vapor-phase reactants, organic solvents and solid waste.

Nevertheless, a Quality Plan will be developed that identifies quality control criteria, including technical performance, safety and environmental performance, in accordance with California and federal regulations. A life cycle analysis will be performed in the Stage 5 development. No potential risks are known at this time. Stage 4 will identify and report any new risks that may arise during the prototype system testing in accordance with Commission requirements and in close collaboration with PIER staff.

Strategic

The project has no known dependencies on other projects under development by PIER or elsewhere. It is strategically placed with respect to the existing thin-film technologies. It offers a unique technology to circumvent current energy problems in California and is not dependent on other PIER projects.

Production Readiness

The EMLE project presents the industry with an inexpensive, user-friendly, environmentally benign route for high volume production of PV modules. Process development in stage 4 will lead to production readiness. Collaboration with our partner CIS Solartechnik, GmbH, for electrodeposition of CIS modules is presently underway for ‘building integrated PV’ application. When developed, the EMLE method will already have a marketing vehicle in place for this technology. The revolutionary attributes of the EMLE project present an exciting opportunity to investors. Other potential commercializing partners include the electric utility companies and the CIS PV industry. The partnerships with the PV industry will strengthen the project and facilitate the final market transfer of the technology. We plan to select a commercializer and obtain commercializing partner commitment in stage 4. Advancing the project to stage 4 will greatly enhance the project's commercial viability and success.

Public Benefits / Costs

The electricity consumer is the end user and thus ultimate beneficiary of the project technology. The project will accelerate the commercialization of environmentally safe and reliable PV energy conversion products into the marketplace. It will thus provide access to a clean, affordable, inflation-proof resource to tap into the sun’s energy which in turn will impact the quality of life in California.

The benefits offered by the EMLE technology far outweigh the California Energy Commission cost outlay for the project. The savings in subsidies, lower energy prices, numerous environmental benefits and scientific innovation will have far-reaching effects well into the future and significantly increase the public benefit-cost ratio. Further development of project technology to stage 4 will demonstrate its full potential.

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Appendix I

Details of Project Outcomes

List of Figures

List of Tables

Task 1 - Design and Testing and Optimization of Deposition Apparatus

Task 1 is the key task for this project. It designed, fabricated and assembled a completely new experimental set-up for EMLE deposition. This involved design, development and implementation of rather complex and elaborate apparatus based on a set of new concepts for the deposition of compound semiconductor films. The final version of the deposition equipment for EMLE is shown in Fig.1. Its principal components include:

1. A thin layer flow cell, constructed with the assistance of Eltron Research.
2. A three-way solenoid distribution valve and a Masterflex perilstatic pump comprising a variable speed L/S pump drive, an 'Easy-Load' pump head, tubing, connectors and adapters obtained from Cole-Palmer Instrument Co, for delivery and exchange of solutions with the deposition chamber.
3. Electrolyte reservoirs and waste electrolyte container connected to the deposition chamber through feed lines.
4. Powerlab potentiostat recording-control unit, and process control software from ADInstruments to synchronize the pumping, delivery, equilibration, deposition and monitor the deposition parameters.

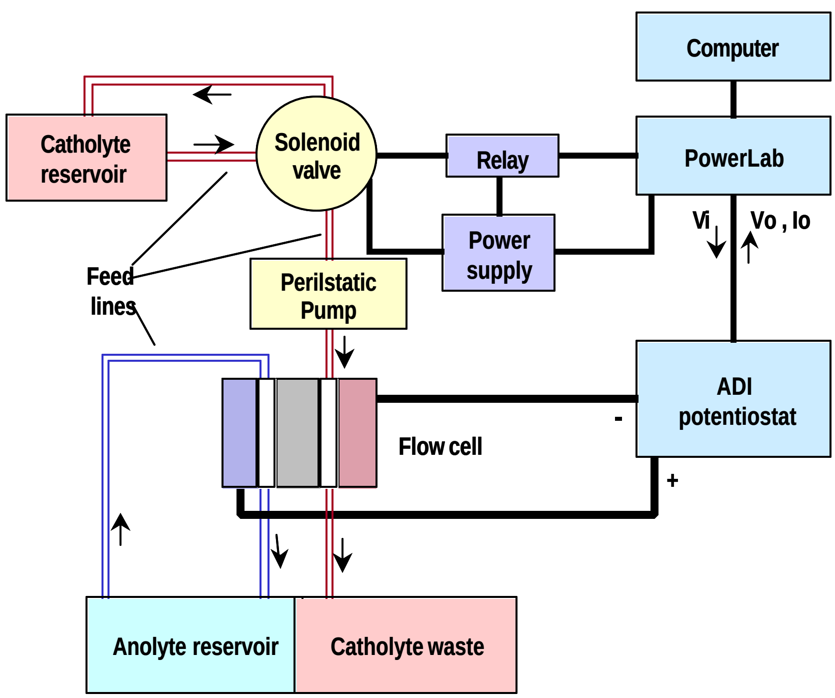

Figure 1. Schematics of experimental set-up developed for EMLE synthesis

The flow cell is the central element of the experimental apparatus. It provides a large surface area electrode and a narrow gap for solution flow through the cathode compartment. The narrow gap confines the reactant ions within a thin solution layer, which establishes equilibrium instantly with the electrode surface. It provides each reactant ion immediate access to the electrode surface for uniform nucleation, promoting epitaxy. Quiescent deposition avoids mass transport and flow pattern complications, thus preventing 3-dimensional nucleation and polycrystallinity.

A separator membrane separates the anode compartment. The anolyte is circulated through a separate circuit to prevent interference from anode reaction products. The solenoid valve controls the flow of the catholyte into the cell. The pump speed regulates solution flow rate. A delay time introduced after each filling equilibrates the electrolyte and avoids mass transport effects. The catholyte flushes out after the deposition of a molecular layer. The anolyte solution is circulated in a closed circuit, to prevent gas accumulation in the anode compartment. The substrates used were Mo/glass, C, Au or Pt coated Cu foils. The counter electrode was Mo/glass, Pt or Ti foil. SCE or a Cu wire measuring the solution redox potential served as reference electrodes.

The earlier part of the project period was devoted to testing the experimental set-up and configuring the PowerLab software: Echem, Chart and Scope, for EMLE application. A series of voltammetric experiments were also performed with the various electrode materials in Cu^{2+} and Se^{4+}/Cu^{2+} solutions in the thin layer and conventional electrochemical cells.

Task 2 - Deposition Parameters and Reaction Mechanism for Cu-In-Se system

Many alternate reaction paths and products can occur in an electrolyte comprising Cu^{2+}, In^{3+} and Se^{4+} ions. The compounds formed depend primarily on the reaction potential (E) and to a large extent on the relative metal ion concentration ratio, $[Cu^{2+}]:[In^{3+}]:[Se^{4+}]$ in the electrolyte.

Fig. 2 illustrates some likely pathways to CIS film formation in an acidic electrolyte containing $[Se^{4+}] \approx [Cu^{2+}] < [In^{3+}]$. The film formation reactions in the ternary system take place in two potential steps, E_1 and E_2. The Cu^{2+} and Se^{4+} species reduce simultaneously to CuSe at E_1 when the $[Se^{4+}]/[Cu^{2+}]$ ratio is ~ 0.8 [8]. Cu_2Se or Se may co-deposit when $[Se^{4+}]/[Cu^{2+}]$ < or > 0.8, respectively . The CuSe film reduces to Cu_2Se and Se^{2-} at a more reducing potential, E_2. The Cu_2Se and Se^{2-} react with the In^{3+} from the solution *via* homogenous chemical reaction C, to form a $CuInSe_2$ film. Alternately, the Se^{2-} may chemically react with the Se^{4+} in the electrolyte to form Se^0 (C") or react with In^{3+} to form In_2Se_3 (C').

Controlling the kinetics of competing reactions is essential to obtain a stoichiometric film. The EMLE approach controls kinetics by limiting the solution volume in addition to the standard parameters, e.g., temperature, electrolyte composition and deposition potential [6].

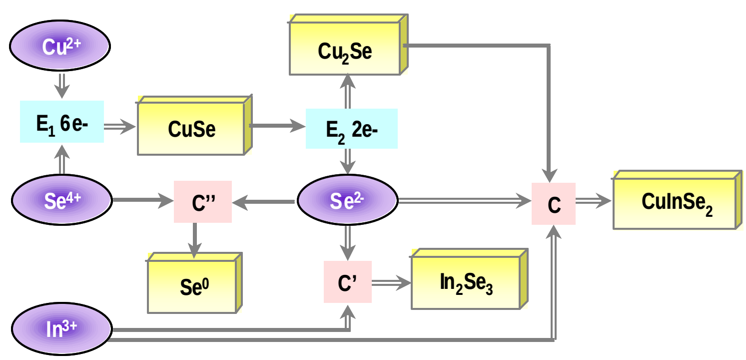

Figure 2. Mechanism of formation of Se, CuSe, Cu_2Se and $CuInSe_2$ films from a solution containing Cu^{2+} In^{3+} and Se^{4+}ions.

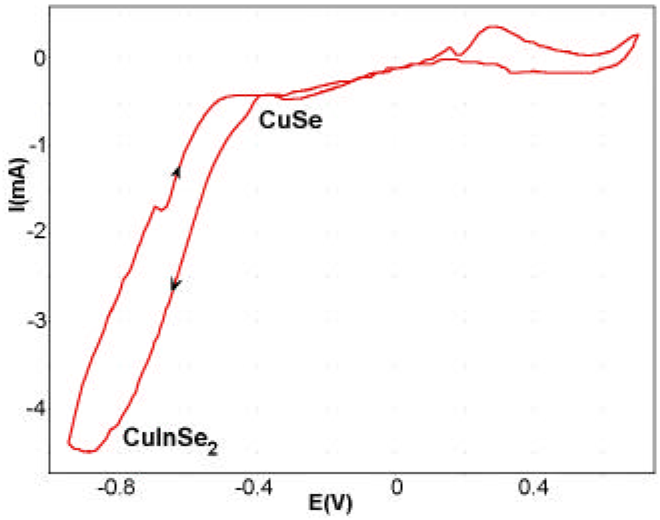

Figure 3. Voltammogram in 5mM Cu^{2+}+15mM In^{3+}+8.6mM Se^{4+} + 0.3M K_2SO_4 at a C disk rotating at 400 rpm, scan rate 10 mV/s.

The standard experimental parameters for EMLE deposition: temperature, electrolyte composition, deposition potential, equilibration time and layer deposition time, were investigated by conducting *in-situ* coulometric and voltammetric studies of redox reactions for Se^{4+}, Cu^{2+}, Se^{4+}/Cu^{2+} and $Se^{4+}/Cu^{2+}/In^{3+}$ electrolyte systems using a conventional cell, as well as the thin layer deposition cell. An important result involves the underpotential formation of CuSe at potentials nearly 500mV positive of the Cu-Se codeposition potential. This appears possible even on an ordinary platinized Ti surface following Se formation during anodic oxidation.

The voltammograms in Figs. 3 and 4 distinguish the processes occurring in bulk solution and a thin electrolyte layer for the Cu-In-Se system in sulfate solutions. The cyclic voltammogram in Fig. 3 was obtained in a conventional large volume (200ml) cell at a carbon rotating disk electrode. The curve shows two reduction steps at E_1 and E_2 to form CuSe and $CuInSe_2$. During the cathodic scan the CuSe formed at E_1 converts to $CuInSe_2$ at E_2. Upon reversing the scan direction, the $CuInSe_2$ film continues to grow in the region $-1.0 < E < -0.6$V. A CuSe layer forms on top of the $CuInSe_2$ film in the region $-0.5 < E < 0$V. This Cu_xSe film dissolves during the anodic segment at $0 < E < 0.4$V. The dissolution of $CuInSe_2$ starts at $E > 0.6$V.

Fig. 4 shows the cyclic voltammograms obtained in the limited volume of the flow cell cathode compartment containing a $Cu^{2+}/In^{3+}/Se^{4+}/K_2SO_4$ solution. The anode compartment was filled with the supporting electrolyte. The current-voltage curve was obtained under quiescent conditions. The curve segment going cathodic from 0V shows a 2-step reduction as in Fig. 3 for CuSe formation at $-0.2V < E < -0.4V$ and $CuInSe_2$ formation at $E < -0.5V$. On scan direction reversal, the current output appears different from that in Fig. 3. Film growth is arrested as the thin solution layer depletes of more noble metal ions and the reduction reaction proceeds to form In_2Se_3.

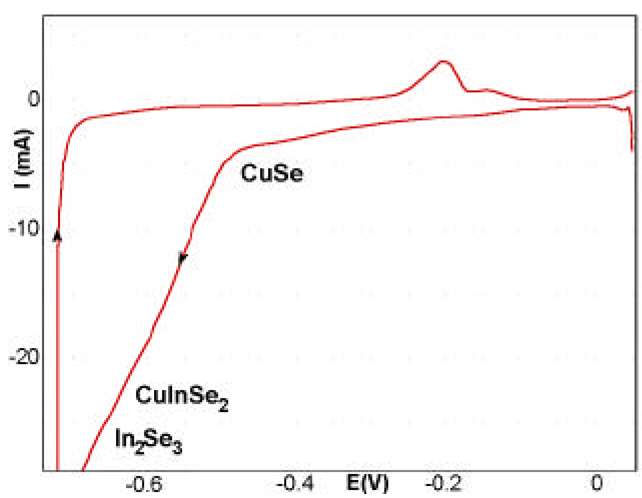

Figure 4. Voltammogram in 3mM Cu^{2+}+10mM In^{3+}+5.6mM Se^{4+}+ 0.3M K_2SO_4 at a Au substrate in thin layer cell, scan rate 10 mV/s.

EMLE for CIS films thus, takes advantage of self-limiting reactions and the low free energy of -254kJ/mol [13] for CIS formation to control the stoichiometry. Theoretical treatment for compound formation has been presented by Kroger [14]. A monolayer of compound can deposit at a more positive potential than (I) one or (II) both component elements of the compound. Thus CIS monolayer forms at a more positive potential than at least one component element, e.g., In. Under the experimental condition used in the flow cell, deposition of In_2Se_3 and then In eventually takes place as the Cu^{2+} and Se^{4+} ions become depleted. The Cu, In and binary phases can be re-dissolved anodically at a less positive potential than that for ternary CIS and Se films.

Task 3 - EMLE synthesis of CuSe and $CuInSe_2$ thin-films

<u>CuSe</u>: The CuSe superlattice films were grown using (a) Conventional cell under quiescent condition, (b) Conventional cell with intermittent stirring, and (c) Thin layer cell using flow, equilibration and deposition sequence. The process parameters — potential limits, substrate pre-anodization, scan rate and temperature — were identified from voltammetric investigations.

<u>$CuInSe_2$</u>: The voltammetric data for $Cu^{2+}/In^{3+}/Se^{4+}$ redox reactions in Figs. 3 and 4 provided the process parameters for CIS deposition. The CIS films were grown with a computer controlled flow, equilibration and deposition sequence. The molecular layers were deposited from a 0.3M K_2SO_4 solution containing 3mM Cu, 10mM In and 5.6mM Se at pH 2. The films were grown under quiescent conditions from bulk solution or thin solution layer. Molecular layer deposition was monitored by tracking the current transients during deposition. This provided information on the nucleation, growth kinetics, dissolution and conductivity of the layers. The information was used to control the electrolyte flow (or stirring) rate and equilibration time.

Fig. 5 shows typical waveforms at a Mo/glass electrode using a conventional cell with intermittent stirring between layer deposition. A 1s digital pulse to a mechanical stirrer and delay periods of 4s and 0.5s simulate the flow and equilibration steps for the conventional cell. This pulse was synchronized with the 0.5s applied potential pulse, which alternated between the equilibrium potential (E_0) and CIS formation potential (E_2). This generated a current output with an initial value of 15mA decaying to ~ 5mA. A small anodic current, observed as the voltage pulse switched to E_0, probably dissolved the binary phases in the film.

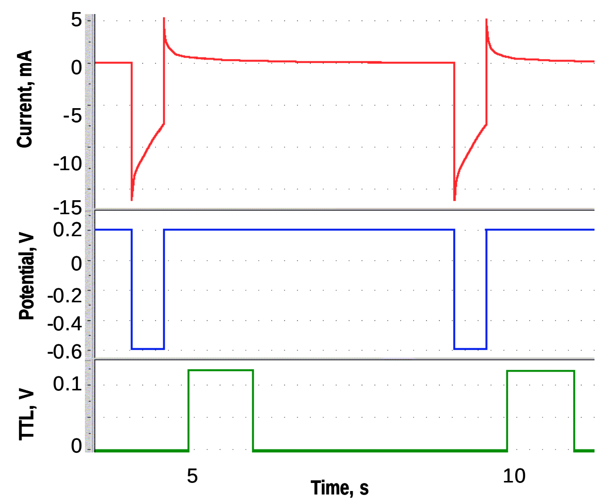

Figure 5. Current output generated with synchronized potential pulses, digital pulsed stirring and equilibration in bulk solution.

Fig. 6 shows similar waveforms obtained for EMLE in a flow through cell. The substrate was $9 cm^2$ Pt coated Cu plate. A 1s digital pulse to the solenoid valve, Fig. 1, initiated solution flow to the cell and solution equilibrated at 4s and 0.5s. This pulse was synchronized with the 0.5s applied potential pulse, which alternated between E_0 and E_2. This generated a current output with an initial value of 30mA decaying to ~ 18mA. Relatively large anodic current spike and small anodic peaks were observed at E_0 (0V), indicating dissolution of binary phases, as anticipated from Fig. 4.

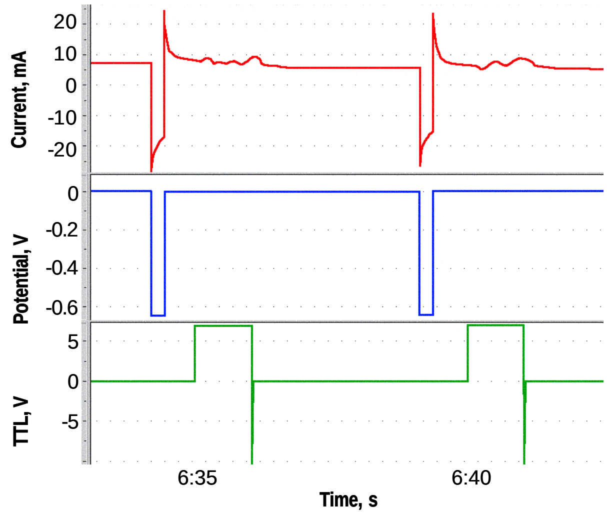

Figure 6. Current output generated with synchronized potential pulses, digital pulsed solution flow, equilibration in flow cell.

Task 4 - Characterization of Electrosynthesized Films

This first study of EMLE synthesis explored a variety of experimental parameters for EMLE deposition, including: electrolyte composition, deposition potential waveform, equilibration time, layer deposition time, temperature, stirring or flow rate between layer deposition. A series of samples comprising 500-800 layers were deposited on Mo/glass by varying waveforms and process parameters. The film composition was determined with electron microprobe analysis using a 10 keV electron beam.

Table I lists the process parameters, E, Q (charge/pulse), stirring, temperature and film composition for samples synthesized by EMLE from bulk electrolyte. As predicted by the voltammogram in Fig. 3, the films were multiphase and Cu rich. The number and types of monolayers deposited during each pulse are deduced from the net charge density/pulse and charge density for monolayer of Se, CuSe, Cu_2Se and $CuInSe_2$ monolayers.

Table 1. CIS Deposition Parameters & Composition Analysis

Sample No.	E(dep) V	E(eql) V	Q mC/cm^2	Stir	T °C	Atomic Ratio			No. of Monolayers			
						Cu	In	Se	$CuInSe_2$	CuSe	Cu_2Se	Se
E206	-0.7	Off	3.4	n	25	3	1	7	1.2	1.6	0.0	0.6
E208	-0.7	Off	2.8	y	25	2	1	4	1.8	0.8	0.0	0.2
E208'	-0.7	Off	1.5	y	60	5	1	5	0.5	0.6	0.4	0.0
E209	-0.6	Off	5.5	n	50	2	1	3	3.2	2.3	0.0	0.0
C2151	-0.6	0.2	5.4	y	50	9	1	27	0.6	2.8	0.0	2.0
C2152	-0.6	0.2	8.6	y	50	22	1	60	0.5	5.1	0.0	3.1
C2153	-0.7	0.2	6.6	y	50	3	1	10	2.0	2.4	0.0	2.3
C2161	-0.7	0.2	4.8	y	50	7	1	12	1.0	3.2	0.0	0.6

The series E samples were deposited at (E_2). No potential was applied during equilibration. This waveform generates a cathodic current without anodic spike. Thus E series films contain less CuSe and negligible quantity of Se phase. Intermittent stirring between layer deposition increased the CuSe content in the film. The small amount of Se is a byproduct of reaction C', Fig. 2, that prevails at room temperature.

The C series samples were deposited with potential waveform switching between E_2 and E_0 values. The anodic spike observed at E_0 leads to decomposition of Cu_xSe to CuSe + Se. The CuSe content may be minimized by decreasing the value of E_2 and Q. Experiments underway plan to characterize the CIS films synthesized in the flow cell. These are anticipated to be Cu-poor, according to Fig. 4.